

ABSTRACT

Three processes for the manufacture of polyhedral oligomeric silsesquioxanes (POSS) which utilize the action of bases that are capable of either attacking silicon or any compound that can react with a protic solvent (e.g. ROH, H<sub>2</sub>O etc.) and generate hydroxide [OH]<sup>-</sup>, alkoxide [RO]<sup>-</sup>, etc. The first process utilizes such bases to effectively redistribute the silicon-oxygen frameworks in polymeric silsesquioxanes [RSiO<sub>1.5</sub>]<sub>∞</sub> where ∞ = 1–1,000,000 or higher into POSS nanostructures of formulas [(RSiO<sub>1.5</sub>)<sub>n</sub>]<sub>Σ#</sub>, homoleptic, [(RXSiO<sub>1.5</sub>)<sub>n</sub>]<sub>Σ#</sub>, functionalized homoleptic, [(RSiO<sub>1.5</sub>)<sub>m</sub>(R'SiO<sub>1.5</sub>)<sub>n</sub>]<sub>Σ#</sub>, heteroleptic, and {(RSiO<sub>1.5</sub>)<sub>m</sub>(RXSiO<sub>1.0</sub>)<sub>n</sub>}<sub>Σ#</sub>, functionalized heteroleptic nanostructures. The second process utilizes base to aid in the formation of POSS nanostructures of formulas [(RSiO<sub>1.5</sub>)<sub>n</sub>]<sub>Σ#</sub> homoleptic and [(RSiO<sub>1.5</sub>)<sub>m</sub>(R'SiO<sub>1.5</sub>)<sub>n</sub>]<sub>Σ#</sub> heteroleptic and [(RSiO<sub>1.5</sub>)<sub>m</sub>(RXSiO<sub>1.0</sub>)<sub>n</sub>]<sub>Σ#</sub> functionalized heteroleptic nanostructures from silanes RSiX<sub>3</sub> and linear or cyclic silsesquioxanes of the formula RX<sub>2</sub>Si-(OSiRX)<sub>m</sub>-OSiRX<sub>2</sub> where m = 0–10, X = OH, Cl, Br, I, alkoxide OR, acetate OOCR, peroxide OOR, amine NR<sub>2</sub>, isocyanate NCO, and R. The third process utilizes base to selectively ring-open the silicon-oxygen-silicon (Si-O-Si) bonds in POSS structures to form POSS species with incompletely condensed nanostructures. These processes also afford stereochemical control over X. The three processes result in new POSS species that can undergo additional chemical manipulations to ultimately be converted into POSS-species suitable for polymerization, grafting, or other desirable chemical reactions.

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